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16p.

RAI 323) OTS:

N64 11383 *

CODE-1

Water Recovery Study

(NASA CR 51575)

(NASA Contract No. NASw-520)

Ames Research Center
National Aeronautics and Space Administration

Quarterly Report for April-June, 1963

OTS PRICE

XEROX

MICROFILM

133605 author

August 9, 1963 signed

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ABSTRACT

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Ultrafiltration studies conducted during the report period have centered on the fabrication of membrane filters capable of direct rejection of the urea species present in urine. Membrane filters prepared from specially cast cellulose acetate and cellophane were evaluated in the aforementioned studies. Further experimentation in the optimization of the cellulose acetate membrane filter employed in the ultrafiltration of modified urine was undertaken. The results to date indicate that either prior urea removal or conversion to an ionic derivative such as an ammonium salt show the maximum promise for the ultrafiltration mode of potable water recovery. The latter mentioned conversion of urea to diammonium citrate has again been demonstrated as a suitable pre-treatment in the recovery via ultrafiltration of a water which meets the United States Public Health Service specifications of chloride ion and dissolved solids in a drinking water supply.

AUTHOR

1.0 DISCUSSION OF RESULTS

1.1 Composition of Human Urine

The physiological fluid, urine, is a very complex mixture of organic and inorganic contaminants dissolved in the parent water solvent. The following table indicates the average composition of a normal urine excreted during a 24 hour period.

Table I

Composition of Urine (ref. 1)

Component	Amount / 24 hours
Sugar	0.015 gms.
Ammonia (as NH_4^+)	0.6-1.2 "
Creatinine	0.8-2.0 "
Uric Acid (partially as urates)	0.3-0.8 "
Hippuric Acid	0.7 "
Urea	12 - 35 "
Chloride ion	10 - 15 "
P (as phosphate)	1.2 "
Ca^{++}	0.1-0.3 "
Mg^{++}	0.1-0.2 "
Na^+	2.5-4.0 "
K^+	1.5-2.0 "
S (as organic and ethereal sulfates)	1.2 "

Total volume = 1000 - 1500 ml.

The table clearly indicates urea and mixed inorganic chlorides are the prime contaminants present in urine. As a consequence of the repeated demonstration of successful chloride and unsuccessful urea rejections obtainable with cellulose acetate membranes, the bulk of the problem centers on the successful rejection of the said urea species.

1.2 Ultrafiltration of Urea vs. Urea Derivatives

As table I clearly indicates, the prime contaminant present in human urine is the organic species, urea. As a consequence of

the reactivity of the urea structure, several alternatives in experimental approach to its removal from aqueous solution via ultrafiltration were undertaken. These approaches with their resultant ramifications on the process potential as reflected by experimental data will be discussed independently.

1.2.1 Direct Ultrafiltration of Unmodified Urine (Urea)

As stated earlier the most promising membrane filter prepared to date (from the standpoint of chloride rejection) was fabricated from cellulose acetate via the use of a casting solution containing magnesium perchlorate analogous to the formulation employed by Loeb and co-workers (ref. 2) in the sea water desalination ultrafiltration program. These membranes gave excellent rejection of the ionic species present in urine but failed to successfully reject the molecular urea species.

Considering the ionic sizes as measured in the crystal lattices indicated in Table II below;

Table II

Atomic and Molecular Sizes

Species	Size
Sodium ion, NA^+	0.95 Å (ref. 3)
Chloride ion, Cl^-	1.81 Å (ref. 3)
Urea, H_2NCONH_2	3.0 Å

the marked differences in the capability of the cellulose acetate membrane to reject sodium chloride and urea are unexplainable. It must be noted that the measurements indicated in Table II were made in the crystalline state and as such may be markedly different when the species are present in an aqueous solution such as urine. Referring to the data in Table III, one can see

that chloride ion can be readily rejected by membranes possessing only limited capacity (see Experiments 86C, 89B, in Table III) for concurrent urea rejection. This repeated inequity in efficiency of chloride versus urea rejection may be a consequence of the ability of the former (ionic chloride) to take on a sphere of water and thus increase in size over and above that of the urea species. The increased size resulting from the hydration sphere can thus account for the capability of the cellulose acetate membrane filter to hold back (reject) sodium chloride virtually completely while only partially rejecting the neutral species, urea. This difference in selectivity is discussed in the reference work of Ambard and Trautman (ref. 4). Although several instances of high level urea rejections were obtained (see Table III, Experiments 105B, 113C), the concurrent low fluxes (rate of product water formation) are outside the realm of practicality. Attempts to incorporate urea in the cellulose acetate casting solution in the absence of magnesium perchlorate gave rise to membranes which on occasion yielded high urea rejections though low fluxes. The results of ultrafiltration studies with all acetate and other membranes on synthetic urines (containing sodium chloride and urea) are summarized in Tables III and IV. In view of the repeatedly demonstrated inability to attain high level urea rejections directly, this line of approach will be discontinued.

1.2.2 Ultrafiltration of Modified Urine - Ammonium Salts

As indicated earlier in the project, the conversion of the prime contaminant urea to an ammonium salt is easily accomplished by a relatively rapid sequence of reactions in the two-step

scheme depicted below:

Step I - Enzymatic Hydrolysis of Urea

$$H_2NCONH_2 + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2$$

The aforementioned reaction is catalyzed by small quantities (1 gm./liter of raw urine) of the available crystalline enzyme, urease. At the ambient urea concentration levels, the reaction was determined to be complete in less than 48 hours at room temperature.

Step II - Acidification of Enzymatic Digest (ammonia) Solution

$$NH_3 + HA \longrightarrow NH_4^{\oplus} A^{\ominus}$$

The aforementioned acidification with the hypothetical acid HA is a very rapid step which consumes stoichiometric quantities of the acid employed. For purposes of study citric acid was chosen because of (1) its trifunctionality which allows one to neutralize the ammonia produced in Step I without requiring precise stoichiometric acidification and (2) citric acid is a non-toxic substance and poses no additional problem in the event of membrane rupture and (3) the citrate anion is large and should lend itself to successful ultrafiltration rejection by the cellulose acetate membrane.

The feasibility of the approach outlined above, that is, urease fermentation followed by citric acid acidification, is demonstrated by the data in Table V. In this experiment, a real "in-house" collected urine was enzymatically fermented with urease and the liberated ammonia neutralized with citric acid so as to employ two of the three available acidic hydrogens

available in citric acid. The balanced equation is depicted below:

As shown in Table V, the aforementioned approach led directly to product water which met the United States Public Health Service specifications on chloride ion and dissolved solids allowable in a drinking water supply (ref. 5).

A comparison of Experiment 84A2 in Table V with Experiment 86C in Table III indicates the marked advantage of conversion of the molecular species urea to the ionic species diammonium citrate. Although high chloride ion rejections were attained in both cases, the urea in the unmodified urine was rejected only to the 60% level whereas in the case of the diammonium citrate rejections of the order of 98% were attained. The apparent relative ease of ammonium salt versus urea rejection by cellulose acetate membranes may conceivably be a consequence of the ability of the former ionic species to hydrate water and "grow" in effective size.

In spite of the immediate success attained in the preparation of potable water from pre-treated human urine as shown in Table V, this experimental approach has its limitations. The chemical conversion of urea through ammonia to diammonium citrate is accompanied by an increase in the osmotic pressure of the feed solution. Inasmuch as the driving force for successful ultrafiltration is the difference between the operating pressure and the osmotic pressure it is highly desirable to maintain the

osmotic pressure at as low a level as is possible. With this requisite in mind, the emphasis during the coming report period is delineated in Section 2.0.

Table III

Ultrafiltration of Synthetic Unmodified Urine (Urea) through Cellulose Acetate Membranes

Expt. No.	Cl^- concentration in parts per million		% Cl^- Rejection	Total available NH_3 concentration in ppm		% NH_3 Rejection	Product flux in liters/ft.^{2}/day	Membrane
	Feed	Effluent		Feed	Effluent			
86A	6000	187	97	18090	2650	85	3.41	notes 1,2
86C	6000	74	99	18090	7195	60	8.81	notes 1,2
89B	4232	30	99.9	14281	3406	76	0.62	notes 1,3
94B	4246	132	97	13973	2410	83	2.21	notes 1,2
94C	4246	241	94	13973	2546	82	1.71	notes 1,2
105B	5174	117	98	14977	557	96	0.44	notes 1,4
112C	4102	204	95	13772	3334	76	58.18	notes 1,5
113C	5434	23	99.6	15448	133	99.2	0.65	notes 1,4

Table IV

Ultrafiltration of Synthetic Unmodified Urine (Urea) through Miscellaneous Membranes

Expt. No.	Cl^- concentration in parts per million Feed	Effluent	% Cl^- Rejection	Total available NH_3 concentration in ppm Feed	Effluent	% NH_3 Rejection	Product flux in liters/ft.^{2}/day	Membrane
91A	3842	159.0	96	13760	5680	59	0.95	note 6
91B	3842	0.7	>99.9	13760	-	-	0.13	note 6
91C	3842	201.0	95	13760	8160	41	2.88	note 7
88A	3832	3035	21	13900	12596	9	16.43	note 9
88B	3832	3056	20	13900	12972	7	15.18	note 9
88C	3832	3046	21	13900	12972	7	16.43	note 9
89A	4232	2489	42	14281	8678	39	10.01	note 8

Table V

Ultrafiltration of Real Urine (which was enzymatically fermented and Citric Acid Acidified) through Cellulose Acetate Membranes

Expt. No.	Cl^- concentration in parts per million		% Cl^- Rejection	Total available NH_3 concentration in ppm		% NH_3 Rejection	Product flux in liters/ft.^{2}/day	Membrane
	Feed	Effluent		Feed	Effluent			
84A2	6429	117	98.2	13320	49	99.6	8.35	note 2,10

NOTES TO TABLES III, IV AND V

1 Operating pressures of 2000 ± 100 psi and temperatures of 30°C. ± 1°C. were maintained through the use of a back pressure regulator and constant temperature bath respectively.

2 Cellulose Acetate:Acetone:Magnesium Perchlorate:Water 22.2:66.7:1.1:10.0 casting solution. Quench Time - 3 mins., Annealing Temperature - 82°C. 10 mil drawdown.

3 Commercial DuPont CA 148 Cellulose Acetate Film.

4 Casting solution as in (2) but urea substituted for magnesium perchlorate.

5 Casting solution as in (2) with additional urea added.

6 Potassium salt of a weakly acidic cation exchange membrane.

7 Sodium salt of a strongly acidic cation exchange membrane.

8 Copper ferrocyanide deposited by countercurrent diffusion.

9 Commercial cellophane.

10 Solids - 370 parts per million, below the 500 parts per million allowable by USPHS (ref. 5).

2.0 PROJECTED PROGRAM FOR THE COMING REPORT PERIOD

As the results in Table III clearly indicate, the high level direct urea rejection required for potable water recovery can only be attained at the expense of the rate of product water recovery (flux). Conversely, the conversion of urea through ammonia to diammonium citrate although readily giving use to high initial flux rates and USPHS passable water, suffers in that high yields cannot be attained due to the buildup of osmotic pressure in the latter stages of the batch process. With these considerations in mind, the bulk of the program will be directed toward the removal of the urea from urine as a pre-treatment step. The approach, if successful, will then convert the urine to the equivalent of a dilute (0.1-0.2 molar) chloride-ion containing salt solution of much lower osmotic pressure than raw urine itself. The reduced osmotic pressure should allow one to attain near theoretical recovery yields of the desired water. In view of the 98+% rejections of chloride ion attainable with cellulose acetate membrane filters, studies on the optimization of the flux characteristics through the species will continue.

3.0 PROTOTYPE ENGINEERING CONSIDERATIONS

The successful fabrication and employment of a water recovery system for use in closed ecological systems is a problem of great consequence in the overall aerospace program. With this in mind, a preliminary study in the evaluation of prototype design to meet the following criteria has been undertaken:

a. Minimal weight
b. Minimal volume
c. Minimal power
d. Maximal reliability
e. Maximal maintainability.

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